

A survey of the geophysical properties of chlorinated DNAPLs

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Abstract

Dense Non Aqueous Phase Liquids (DNAPLs) are a family of fluids often encountered as industrial contaminants. Some of the most problematic DNAPLs are chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). While many DNAPLs have been extensively studied from a hydrology perspective, documentation of DNAPL properties relevant to geophysical detection is far from complete. We present a short survey of acoustic velocity, density, and dielectric constant measurements for an important subset of commonly encountered dense chlorinated contaminants. Viscosity and surface tension data are included to allow exploration of contaminant signatures within the context of poroelastic or contact theory models. Where available, the temperature dependence of solvent properties are also provided. Densities for the listed DNAPLs range from 1253 to 1622 kg/m³ at 20 °C. All are effectively non-polar with dielectric constants between 2.2 and 10.9 and have relatively low compressional wave velocities ranging from 938 to 1217 m/s. We conclude with documentation of a small collection of recent experiments investigating the properties of soils partially saturated with similar fluids. Current laboratory evidence demonstrates that DNAPLs can produce changes in geophysically measurable properties. We hope that this survey will facilitate further studies of the feasibility and effectiveness of geophysical techniques for detection of DNAPLs in the subsurface.

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1. Introduction

Dense Non-Aqueous Phase Liquids or DNAPLs are a family of fluids which include some of the most common and problematic groundwater contaminants, present in excess of US Environmental Protection Agency (EPA) toxicity levels at thousands of sites in the US (Pankow and Cherry, 1996). Chlorinated solvents, including trichloroethylene (TCE), tetrachloroethylene (PCE), and carbon tetrachloride, are the most important sub-class of DNAPLs due to their wide-spread use in the electronics, chemical, dry-cleaning, and metal fabrication industries. A variety of geophysical techniques have been proposed for the detection of DNAPLs in the shallow subsurface (Romig, 2000) including ground-penetrating radar (GPR) (Olhoeft, 1992; Brewster and Annan, 1994; Sneddon et al., 2000), seismic techniques (Temples et al., 2001), nuclear magnetic resonance (NMR) (Bryar and Knight, 2003), resistivity methods (Newmark et al., 1997), induced polarization (Grimm and Olhoeft, 2004; Briggs et al., 2004), and spontaneous potential measurements (Minsley et al., 2004). However, most of these methods lack the spatial resolution and/or sensitivity for the direct characterization of small DNAPL lenses or pools. GPR and high-resolution borehole seismic methods (Ajo-Franklin et al., 2002) possess both desired properties when appropriate source frequencies and source/receiver geometries are used. Many DNAPL detection efforts have been motivated in part by the controlled field-scale GPR experiments carried out at the Borden test site. These experiments succeeded in monitoring the downward migration of PCE in situ through a series of pools at depth (Brewster et al., 1992, 1995; Sander et al., 1992; Redman, 1992; Brewster and Annan, 1994) visible as discrete time-varying radar reflectors. While the Borden experiments demonstrated the effectiveness of radar in a monitoring capacity, the ambiguity of reflector interpretation suggested that static detection or characterization of PCE using surface radar might be difficult assuming traditional survey techniques.

In this review we present a short literature survey of acoustic velocity, density, and dielectric constant measurements for an important subset of commonly encountered dense chlorinated contaminants. Viscosity

and surface tension data are included to allow exploration of contaminant signatures within the context of poroelastic or contact theory models. When possible we have provided the results of multiple laboratory measurements and documented the temperature, pressure, and frequency dependence of the examined properties. Preference was given to results from recent papers over handbook values due to the difficulty in determining the conditions and experimental apparatus used for the later class of data. We also include a summary of currently available measurements on the acoustic and dielectric properties of unconsolidated materials partially saturated with a NAPL phase.

Although significant progress has been made using radar or geoelectrical methods for light NAPL (LNAPL) detection (Daniels et al., 1992, 1995; Atekwana et al., 2000) we will confine our discussion to dense chlorinated fluids. We will also neglect electrical conductivity measurements of DNAPL/water mixtures despite increasing evidence that they may be useful for characterizing contaminant plumes. We limit our investigation to DNAPLs largely because they represent a very different class of imaging targets in comparison to LNAPLs due to their deep penetration into the saturated zone. We hope that this survey will facilitate further studies of the feasibility and effectiveness of geophysical techniques for the detection and characterization of DNAPLs in the subsurface.

2. Basic chemical, regulatory, and toxicological properties

Table 1 lists the most commonly used chlorinated solvents ranked by annual production (Pankow and Cherry, 1996) with tabulated values for solubility, US Environmental Protection Agency (EPA) maximum allowable contaminant levels (MCLs), and basic chemical information. Benzene and toluene, two common light NAPL contaminants, and water are included for reference. Because DNAPLs are denser and often less viscous than water (see Table 2), they easily penetrate deep into the saturated zone and pond at low permeability barriers (Kueper et al., 1993). As DNAPLs slowly dissolve in the saturated zone, they produce large plumes of contaminated ground water although

most of the pollutant mass remains in concentrated pools. Generally, contaminated sediments can be divided into zones where DNAPLs exist as a continuous phase, which are typically referred to as regions of free-product, and zones where DNAPLs only exist in a residual form. Both of these states are distinct from the plume of aqueous contamination which typically extends over a much larger region. The distribution of DNAPLs in the subsurface is controlled by a large number of site factors and is strongly influenced by the spatial heterogeneity of permeability and porosity (Lemke et al., 2004). Existing information on the architecture of DNAPL pools has been obtained from numerical simulations (Kueper and Frind, 1991a,b; Kueper and Gerhard, 1995), controlled mesoscale experiments (Kueper et al., 1993), or high resolution push-point fluid sampling (Parker et al., 2003); a detailed model of DNAPL distribution in an uncontrolled field setting has yet to be developed.

The low absolute solubility of most DNAPLs insures that the total pollutant mass mobilizes slowly; some contaminant pools have estimated life-times of several centuries. However, these fluids often have high solubilities relative to EPA toxicity limits making DNAPL plumes long-term groundwater hazards unless properly treated. Most chlorinated solvents have aqueous solubilities 4 to 5 orders of magnitude greater than the EPA's maximum allowable contaminant level (MCL) (see Table 1). Chlorinated solvents also typically have high vapor pressures and low boiling points, properties which facilitate volatilization in the vadose zone.

Although chlorinated solvents vary in toxicity, all have both acute and chronic health effects on humans. PCE is a well studied DNAPL useful as an example of the properties characteristic of chlorinated solvents. PCE is acutely toxic at high levels (Stevens and Eisenmann, 1997), has demonstrated carcinogenic effects in animals and is thought to be a carcinogen for humans (Lucius et al., 1992; Stephenson, 1995). Furthermore, PCE has negative effects on the human reproductive system (Doyle et al., 1997; Sallmen et al., 1998). Carbon tetrachloride, another common DNAPL, is a confirmed hepatotoxin (Faroon et al., 2003; Davidson and Zon, 2003; Manahan, 1994). The degradation byproducts of chlorinated solvents are sometimes as toxic as the original compound, as is the case with vinyl chloride (VC). VC, which precedes ethene in the reductive dechlorination of PCE (Maymo-Gatell et al., 1997), is a relatively potent carcinogen (Brown and Bittner, 1993).

3. The geophysical properties of chlorinated solvents: a survey

Table 2 presents the results of a collection of several acoustic and dielectric measurements on common dense chlorinated solvents. The first eight chemicals are ranked by total U.S. production in 1986 in millions of kilograms (Pankow and Cherry, 1996). Letters following each measurement denote the appropriate reference and experimental conditions found in Table 6. For the purpose of comparison we also present data on two light non-aqueous phase liquids

Table 1
Production levels and physical properties for the most common chlorinated solvents

Compound	Chemical formula	Annual prod. ^a (10 ⁶ kg/yr)	Solubility ^b (in water) (10 ⁻⁶ kg/L)	EPA MCL (10 ⁻⁶ kg/L)	Vapor pressure ^c (Torr)	Boiling point ^d (C)
1,2-Dichloroethane	C ₂ H ₄ Cl ₂	5871	8690	0.005	64	83.5
1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	294	1360	0.2	90	74.1
Carbon tetrachloride	CCl ₄	284	800	0.005	90	76.5
Methylene chloride	CH ₂ Cl ₂	255	20000	0.005	348	40.2
Chloroform	CHCl ₃	191	8000	0.01	160	61.7
Tetrachloroethylene	C ₂ Cl ₄	184	150	0.005	14.2	121.2
Trichloroethylene	C ₂ HCl ₃	75	1100	0.005	57.8	87.2
Benzene	C ₆ H ₆	–	1780	0.005	76	80.1
Toluene	C ₇ H ₈	–	515	1	22	110.6
Water	H ₂ O	–	–	–	17.5	100

Data on benzene, toluene, and water are provided for the purpose of comparison. EPA MCL is an abbreviation for the US Environmental Protection Agency's Maximum allowable Contaminant Level.

^a Pankow and Cherry (1996).

^b Montgomery (1991).

^c Montgomery (1991) at 20 °C.

^d Montgomery (1991).

Table 2
Geophysical properties of common chlorinated solvents

Compound	Density ρ (kg/m ³)	P-wave velocity V_p (m/s)	Bulk modulus K (10 ⁹ Pa)	Dielectric constant κ	Absolute viscosity ^a η (10 ⁻³ Pa · s)	Surface tension ^a T_s (10 ⁻³ N/m)
1,2-Dichloroethane	1238 (a)	1173 (a)	1.703		0.887 [15 °C]	35.3
		1177 (b)		10.08 (b)		
1,1,1-Trichloroethane	1238 (d)	1174 (d)	1.175	10.95 (c)	0.903 [15 °C]	28.28
	1321 (e)	943 (e)		7.252 (f)		
Carbon tetrachloride	1329 (a)	942 (a)	1.335	7.52 (g)	0.965 [20 °C]	29.49
	1584 (i)	918 (i)		2.240 (f)		
Methylene chloride	1594 (h)	935 (h)	1.596	2.241 (j)	0.449 [15 °C]	30.41
		906 (k)		2.213 (k)		
Chloroform	1336 (l)	1093 (l)	1.498	9.14 (j)	0.596 [15 °C]	29.91
	1316 (i)	1052 (b)		8.62 (b)		
Tetrachloroethylene		1053 (m)	1.694	8.72 (m)	1.932 [15 °C]	32.86
	1606 (a)	1027 (a)		4.66 (m)		
Trichloroethylene	1606 (d)	1030 (d)	1.495	2.29 (b)	0.566 [20 °C]	29.5
	1451 (t)	1015 (t)		2.28 (o)		
Benzene	1451 (q)	1014 (q)	1.410	3.335 (t)	0.6028 [25 °C]	28.9
				3.409 (r)		
Toluene			1.527	3.42 (s)	30.90 [20 °C]	
	866 (u)	1276 (u)		2.253 (v)		
Water ^b	879 (h)	1324 (h)	2.192	2.268 (k)	1	72
	866 (h)	1328 (h)		0.552		
	862 (z)	1283 (k)		2.381 (z)		
				2.365 (k)		

Letters refer to experiments detailed in Table 6. Temperatures and measurement frequencies for density, acoustic, and dielectric measurements are also included in Table 6. Bulk moduli are calculated from tabulated velocity and density data ($K = \rho V_p^2$). Temperatures noted below viscosity values apply only to viscosity.

^a Mercer and Cohen (1990).

^b All water measurement values are for distilled DI water.

Table 3
The temperature dependence of density

Compound	Density				Reference
	@ 20 °C (kg/m ³)	A (kg/m ³)	B (kg/(m ³ °C))	Range [pnts] (°C)	
1,2-Dichloroethane	1252.9	1282.5	-1.482	25–40 [4]	(ah)(ai)
1,1,1-Trichloroethane	1338.1	1370.7.1	-1.632	0–60 [8]	(aj)(ai)
Carbon tetrachloride	1594.1	1632.7	-1.929	0–50 [6]	(h)
Methylene chloride	1325.7	1363.9	-1.910	25–35 [3]	(i)
Chloroform	1488.6	1526.7	-1.908	0–50 [6]	(h)
Tetrachloroethylene	1622.2	1655.1	-1.647	24–42 [10]	(ak)(n)
Trichloroethylene	1464.1	1498.1	-1.678	18–42 [14]	(aj)(ae)
Benzene	879	900.4	-1.072	10–50 [5]	(h)
Toluene	866	884.6	-0.940	0–50 [6]	(h)
Water	998.2	1001.9	-0.2	0–30 [4]	(z2)

A and B are fitting coefficients for the linear models (see Eq. (1)).

All curves were interpolated/extrapolated to 20 °C for comparison (column 2). Range column indicates the range of temperatures used for the linear fit and the number of measurement points.

Table 4
The temperature dependence of acoustic velocity

Compound	Acoustic velocity				Reference
	@ 20 °C (m/s)	A (m/s)	B (m/(s°C))	Range [pnts] (°C)	
1,2-Dichloroethane	1217	1297	−4.0	30–40 [2]	(b)
1,1,1-Trichloroethane	–	–	–	–	–
Carbon tetrachloride	938.6	1004	−3.27	0–50 [6]	(h)
Methylene chloride	1089	1163	−3.7	20–30 [2]	(b)
Chloroform	1001.4	1070	−3.44	0–50 [6]	(h)
Tetrachloroethylene	1059	1125	−3.3	30–40 [2]	(b)
Trichloroethylene	1050	1120	−3.5	30–40 [2]	(b)
Benzene	1325.9	1421	−4.75	10–50 [5]	(h)
Toluene	1322.7	1414	−4.29	0–50 [6]	(h)
Water	1482.3	1407	3.55	0–30 [4]	(z2)

A and B are fitting coefficients for the linear models (see Eq. (1)). All curves were interpolated/extrapolated to 20 °C for comparison (column 2). Range column indicates the range of temperatures used for the linear fit and the number of measurement points.

(toluene and benzene) and water. When listed, all water values are for distilled DI water (Anderson et al., 2000). In field conditions where some amount of dissolved salts are almost always present, corrections for salinity should be applied.

Tables 3, 4 and 5 document a smaller subset of experiments which provide insight into the temperature dependence of density, acoustic velocity, and dielectric constant for the same fluids. Measurement sets were individually fit using linear models and the resulting coefficients are included. Almost all of the datasets examined exhibited linear temperature and pressure dependence within the range of environmental conditions relevant to near-surface measurements.

Table 6 provides the reference codes and information on the condition under which each measurement

was performed if an experimental description was available. In addition to fluid temperature, we also provide the frequency of both the acoustic and dielectric measurements.

3.1. Acoustic properties

The most basic parameters for understanding the seismic response of a fluid are density (ρ) and compressional wave velocity (V_p). Within the geophysics community, little attention has been paid to the acoustic properties of DNAPLs; the most studied fluids besides water are the light hydrocarbons present in petroleum mixtures (Wang and Nur, 1991). The existing database of acoustic velocity values for chlorinated solvents are found almost entirely within the physical chemistry and

Table 5
The temperature dependence of dielectric constant

Compound	Dielectric constant				Reference
	@ 20 °C	A	B (1/°C)	Range [pnts] (°C)	
1,2-Dichloroethane	10.95	11.977	−0.0506	10–45 [8]	(c)
1,1,1-Trichloroethane	7.242	7.962	−0.0360	5–20 [4]	(f)
Carbon tetrachloride	2.240	2.281	−0.0020	3–22 [14]	(f)
Methylene chloride	9.140	10.014	−0.0433	0–40 [5]	(j)
Chloroform	4.841	5.212	−0.0185	0–50 [6]	(j)
Tetrachloroethylene	2.297	2.365	−0.0034	25–30 [2]	(o)
Trichloroethylene	3.409	3.525	−0.0062	16–30 [3]	(r) (k)
Benzene	2.284	2.312	−0.0014	14–50 [5]	(ab)
Toluene	2.38	2.420	−0.0020	15–35 [3]	(af)
Water	80.10	87.164	−0.3465	5–55 [10]	(ag) (g)

A and B are fitting coefficients for the linear models (see Eq. (1)). Note that κ is dimensionless. All curves were interpolated/extrapolated to 20 °C for comparison (column 2). Range column indicates the range of temperatures used for the linear fit and the number of measurement points.

Table 6
Reference codes and experimental conditions

Code	Cite	Temp. (C)	EM freq. (10 ⁶ Hz.)	Aco. freq. (10 ⁶ Hz.)
a	Krishnaiah and Surendranath (1996)	30	–	2
b	Nath and Saini (1990)	30 [30:40, 2]	1.8	2
c	Corradini et al. (1996)	20 [– 10:80, 17]	2	–
d	Kumari et al. (2002)	30	–	4
e	Sekhar et al. (2001)	30	–	4
f	Loon et al. (1967)	19.8 [– 25:19.8, 10]	0.1	–
g	Dean (1992)	20	*	–
h	Freyer et al. (1929)	20 [0:50, 6]	–	0.414
i	Aminabhavi and Banerjee (1998)	25 [25:35, 3]	–	0.004
j	Morgan and Lowry (1930)	20 [– 30:70,11]	0.1	–
k	Nath and Dubey (1980)	30 [30:40,2]	1.8	2
l	Lagemann et al. (1948a)	20	–	0.5
m	Nath and Tevari (1992)	30 [20:30,2]	1.8	2
n	Venkatesulu et al. (1997)	30 [30:40,2]	–	–
o	Nath and Narain (1982)	25 [25:35,2]	1.8	–
p	Nath and Dixit (1984)	25 [25:35,2]	–	2
q	Iloukhani et al. (1999)	30	–	1
r	Timmermans et al. (1955)	20	0.5	–
s	Walden and Werner (1924)	16	36 (*)	–
t	Nath (1995)	30	1.8	3
u	Weïssler (1949)	30	–	3
v	Sastry et al. (1999)	35	3	–
w	Pellam and Galt (1946)	21.8 [7.5:21.8,2]	–	15
x	Nath and Singh (1986)	30 [30:40,2]	–	2
y	Ritzoulis et al. (1986)	25 [15:25,3]	2	–
z	Mopsik (1969)	25 [– 50:25,4]	*	–
z2	D'Arrigo and Paparelli (1987)	20 [– 40:30,8]	–	10
z3	Al-Azzawi et al. (1990)	20 [25:55,4]	1	–
ab	Akhadov (1980)	[14:50.3,5]	*	–
ac	Mussari et al. (2000)	[25:30,2]	–	–
ad	Lorenzi et al. (1996)	[16:40,2]	–	–
ae	Prasad et al. (2002)	[30:50,3]	–	–
af	Moumouzias and Ritzoulis (1997)	[15:35,3]	2	–
ag	Anderson et al. (2000)	[5:55,10]	25–250	–
ah	Joshi and Aminabhavi (1990)	[25:40,4]	–	–
ai	Sivaramprasad et al. (1990)	[30:60,4]	–	–
aj	Anon (1973)	[0:60,8]	–	–
ak	Comelli and Francesconi (1991)	[24:42,10]	–	–
aj	Francesconi and Comelli (1990)	[18:42,14]	–	–

Where measurements at multiple temperatures are available, the [C:D,N] notation denotes N measurements ranging from temperature C to temperature D. The first number in the temperature column corresponds to the measurements conditions for the experimental values in Table 2. Columns 5 and 6 include the frequencies utilized for the specified electromagnetic (EM) or acoustic (Aco.) measurement. References where measurement frequency were unclear or not specified are marked with a*.

chemical engineering literature; most of the papers cited measure pure solvent velocities as end-members of binary and ternary mixture experiments. The majority of the measurements use interferometric methods at ultrasonic frequencies, typically between 1 and 3 MHz. Freyer et al. (1929) describe an early interferometric instrument operating at 0.4 MHz. A smaller number of experiments use time domain techniques; Pellam and Galt (1946) use a pulsed reflection measurement apparatus to make both velocity and attenuation measurements at 15 MHz. Eggers and Kaatze

(1996) provide an excellent review of ultrasonic measurement techniques for liquids, including both CW and pulse methods. Densities are commonly measured using pycnometers or vibrating tube densimeters.

For the chlorinated solvents examined, the ultrasonic velocities ranged between 939 and 1217 m/s at 20 °C (see Table 4), considerably slower than the speed of sound in pure water (\approx 1480 m/s). The densities were higher than that of water, with 1,2-dichloroethane being the lightest at 1253 kg/m³ and PCE the densest at 1622 kg/m³ (see Table 3). Table 2 includes dynamic bulk

moduli calculated from the most recent and consistent combination of velocity and density data using $K = \rho V_p^2$. Table 2 also includes fluid viscosity to allow easy calculation of the poroelastic properties of solvent saturated soils.

Tables 3 and 4 detail the temperature dependence of density and acoustic velocity for the same solvents. For each fluid, multiple measurements were fit using a linear relation of the form,

$$P(T) = A + BT \quad (1)$$

where A and B are fitting coefficients, P is the property being investigated, and T is temperature in °C. For all of the DNAPLs discussed in this paper, V_p and ρ decrease with increasing temperature. For the density fits, B , the gradient of ρ with respect to T , were between -1.649 and $-4.3 \text{ kg/m}^3 \text{ } 1^\circ\text{C}$ for the chlorinated solvents. B values for V_p were between -3.3 and $-4.75 \text{ m/s } 1^\circ\text{C}$. Interestingly, the B coefficient for water displays the opposite sign with V_p increasing with temperature. Column 2 of Tables 3 and 4 are extrapolations of the linear models to 20°C to allow easy comparison between fluids. Column 5 of Tables 3 and 4 specify the range of temperatures for which property values were available with the number of measurements used for the fit specified in brackets. Although most of the solvents listed have a linear temperature dependence in the range of 5 to 50°C , some caution should be used in applying these relations, particularly for the fits which used a small number of data points.

For both velocity and density measurements, temperature control for recent studies is on the order of $\pm 0.01^\circ\text{C}$ (Nayak et al., 2003; Sekhar et al., 2001; Comelli and Francesconi, 1991; Choudary and Naidu, 1982) with slightly larger error bars for older experiments, $\pm 0.05^\circ\text{C}$ (Weissler, 1948; Lagemann et al., 1948b). Uncertainties in density measurements vary but are generally below 0.2 kg/m^3 (Nayak et al., 2003; Comelli and Francesconi, 1991; Joshi and Aminabhavi, 1990; Nath and Dixit, 1984). Errors in velocity measurements are somewhat higher, but still typically below $\pm 2 \text{ m/s}$ (Nayak et al., 2003; Sekhar et al., 2001; Nath, 1995; Nath and Dixit, 1984; Lagemann et al., 1948b).

Acoustic velocity and density were observed to increase with increasing pressure for all of the solvents for which data were available; see the excellent reviews by Oakley et al. (Oakley et al., 2003a,b) and the early experimental paper by Swanson (1934) for pressure data on chloroform and carbon tetrachloride. Bobik (1978) measured pressure dependent velocity changes in benzene on the order of $4.76 \text{ m/s } 1/\text{MPa}$ between 0 and 20 MPa at 17°C , a low enough gradient to allow

neglecting pressure effects on V_p in near-surface environments. Pure fluid attenuation measurements (Pellam and Galt, 1946; Heasell and Lamb, 1956) are not tabulated here but are typically very small in comparison to the intrinsic attenuation of near-surface materials, particularly between the quasistatic state and 10 MHz where few molecular relaxation mechanisms occur. Direct measurements of velocity dispersion in pure liquids are relatively rare, particularly for low frequencies, but existing data suggests that the frequency dependence of acoustic velocity in pure chlorinated solvents is almost insignificant below 50 MHz . Andreae (1957) provides velocity dispersion data from a variety of sources for methylene chloride between 7.54 and 209 MHz at 25°C . Over the decade from 7.54 to 70 MHz he observed a change in velocity of only 5 m/s . More significant velocity changes occur in methylene chloride near a relaxation peak at approximately 480 MHz (Andreae et al., 1960). Cartensen (1954) measured acoustic velocity dispersion between 0.3 and 10 MHz in water, a natural oil (LNAPL), and condensed milk at 32°C . For both the water and oil samples less than 1 m/s variation in acoustic velocity occurred over the decade from 1 to 10 MHz .

3.2. Dielectric properties

One of the most essential parameters for understanding the electromagnetic (EM) signature of a fluid is the relative dielectric permittivity or dielectric constant. The complex frequency dependent dielectric constant (κ^*) can be written as the sum of a real dielectric constant (κ'), a high frequency loss term due to relaxation effects (κ''), and a DC conductivity term (σ_{dc})

$$\kappa^* = \kappa' + i \left[\kappa'' + \left(\frac{\sigma_{dc}}{2\pi f \epsilon_o} \right) \right] \quad (2)$$

where f is frequency, and ϵ_o is the permittivity of free space. In cases with low conductivity, high measurement frequencies, and a small κ'' loss term, the second term in the RHS of Eq. (2) is negligible and $\kappa^* \sim \kappa'$. The values reported in the experimental papers referred to in this section are for κ' , although several provide auxiliary data for κ'' . At low frequencies dielectric properties are typically measured using capacitance bridges (von Hippel, 1954) while resonant cavities (Goodwin et al., 1996; Anderson et al., 2000) and network analyzers (Kremer and Schonhals, 2003) are used in the MHz range.

All DNAPLs are effectively non-polar insulators with dielectric constants at room temperature ranging from 2.24 for carbon tetrachloride to 10.95 for 1,2-dichloroeth-

ane. Displacement of water, a polar fluid with a dielectric constant of 80 at 20 °C, is largely responsible for generating the radar signatures observed in the field. Table 5 summarizes the sensitivity of dielectric constant to variations in temperature. All of the solvents examined exhibit decreasing dielectric constants as a function of increasing temperature. Available temperature data were fit to the same linear model as Eq. (1), with the B coefficient again indicating the gradient of dielectric constant with respect to temperature. The value of B is relatively small for the chlorinated solvents (-0.002 to -0.05) in comparison to that of water (-0.346). Typical errors in dielectric constant measurement vary but are generally under ± 0.05 (Nath and Dubey, 1980; Nath, 1995).

Dielectric constants were observed to be weakly dependent on pressure. Mopsik (1969) measured the pressure dependence of carbon tetrachloride's dielectric properties; fitting a linear model to his data at 25 °C yields a gradient of 0.0016 per MPa, a value small enough to be negligible in near-surface scenarios. For pure chlorinated solvents, no significant variation in κ' occurs between 10 kHz and 1 GHz. von Hippel (1954) presents frequency dependent dielectric values for tetrachloroethylene and carbon tetrachloride; in both cases κ' is constant between 100 Hz and 3 GHz.

3.3. DNAPLs in the field

While the properties of pure DNAPLs are well understood, the contaminants found at most environmental sites are complex mixtures containing both the original substances and the products generated by weathering and biodegradation. Often, existing documentation of the waste disposal process are vague enough to lack utility in the prediction of DNAPL properties; in many sites both the volume and original components of the contaminant are unknown. Sampling and chemical analysis of DNAPLs from monitoring wells can provide clues as to the geophysical properties of the contaminants in situ. In the ideal case, comprehensive lab scale geophysical measurements would be made on extracted DNAPL samples to establish the properties of the contaminant before acquisition of field data. In practice, many sites do not have DNAPL samples for analysis (hence the need for detection) and even in cases where samples do exist they are often destructively analyzed for information on chemical composition and are not available for geophysical measurements. Since the values tabulated within this document are for pure DNAPLs, they should be applied with caution when attempting to analyze field observations.

4. DNAPL/soil mixtures

Although the goal of this survey is to tabulate fluid properties, examination of the electromagnetic and acoustic properties of soil/DNAPL composites is of equal importance; we present an incomplete collection of existing theoretical and laboratory papers on this topic below. Included are some papers detailing LNAPL saturation experiments which may be relevant to investigation of denser solvents because of their similar dielectric properties and low P-wave velocities. We will focus on conclusions relevant to DNAPLs in water saturated sediments since DNAPLs are typically found below the water table. Table 7 provides a brief summary of the included experimental studies.

4.1. Acoustic properties

The acoustic properties of NAPL saturated granular media have not been heavily investigated; however, a small but growing body of experimental results exists

Table 7
Summary of laboratory measurements of NAPL/soil mixtures

Reference	Measurement type	Saturating fluids	Measurement frequency
Geller and Myer (1995)	Acoustic	Freon-113 <i>n</i> -dodecane <i>iso</i> -octane	500 kHz
Porokhovi et al. (1996)	Dielectric	Benzene Heptane Xylene Toluene Acetone	200 MHz– 1.2 GHz
Santamarina and Fam (1997)	Dielectric	Benzene Xylene Toluene TCE PCE Chlorobenzene	200 MHz– 1.3 GHz
Kowalsky et al. (1998)	Acoustic	<i>n</i> -dodecane	90 kHz
Seifert (1998)	Acoustic	Silicone oil Castor oil <i>n</i> -dodecane	900 kHz
Seifert et al. (1999)	Acoustic	Silicone oil	900 kHz
Persson and Berndtsson (2002)	Dielectric	SFSO	10 MHz– 800 MHz
Francisca and Rinaldi (2003)	Dielectric	Paraffin	20 MHz– 1.3 GHz
Geller et al. (2003)	Acoustic	Lubricant oil TCE Toluene	500 kHz
Ajo-Franklin et al. (2004)	Dielectric	TCE	10 MHz– 800 MHz

for synthetic systems (glass beads), clean sands, and natural aquifer cores at low pressures. All laboratory experiments to date have shown that NAPL saturation reduces P-wave velocity and increases P-wave attenuation at frequencies between 60 and 1000 kHz for samples initially saturated with water.

Geller and Myer (1995) investigated the relationship between NAPL saturation, P-wave velocity, and attenuation using 1,1,2-trichloro-1,2,2-trifluoroethane (freon-113), *n*-dodecane, and *iso*-octane as model contaminants. They made measurements on medium sub-rounded quartz sand samples (212–250 microns) with porosities of 42% at effective pressures of 140 kPa. Measurements examining both NAPL injection into water saturated samples and purely NAPL saturated samples were made using an ultrasonic pulse transmission system operating at a central frequency of 500 kHz. Reductions in V_p of up to 40.3% were observed for sands fully saturated with freon-113.

Seifert (1998) and Seifert et al. (1999) performed a similar set of measurements with a focus on varying fluid viscosity and wetting properties. P-wave velocity and attenuation were measured while saturating with two different grades of silicone oil (10 and 100 cs), castor oil, and *n*-dodecane. Seifert used the same sub-rounded quartz sand examined by Geller and Myer (1995) (212–250 microns) but packed the samples to 35% porosities and used a higher effective pressure (690 kPa). Only pure phase measurements were made for the oils while *n*-dodecane was examined during both NAPL-to-water and water-to-NAPL injections. Measurements were made using a similar ultrasonic pulse transmission system operating at a central frequency of 900 kHz. Reductions in V_p of up to 28.8% were observed for sands fully saturated with 10 centipoise silicone oil.

On a slightly larger scale, a series of physical model (0.61 m tank) experiments was performed by Kowalsky et al. (1998). In this experiment, *n*-dodecane was injected into a homogeneous sandpack maintained at a confining pressure of 140 kPa. Acoustic waveforms were acquired using a miniature accelerometer array and bar piezoelectric source operating at a frequency of 60 kHz. The resulting dataset was processed using a 2D straight-ray tomographic algorithm. The velocity decrease due to *n*-dodecane saturation appeared to be only 2% for the rays of maximum delay. However, amplitude anomalies of up to 65% were observed along high delay paths. Geller et al. (2000) performed a similar experiment, using the same apparatus operating at 90 kHz, to image a lens of *n*-dodecane pooled at a capillary barrier. They observed reductions in amplitude and an increase in traveltimes for rays traveling through

the NAPL zone. Subsequent asymptotic waveform tomography performed by Keers et al. (2000) revealed peak velocity reductions on the order of 2.5%.

Geller et al. (2003) examined the effects of toluene and trichloroethylene (TCE) saturation on ultrasonic P-wave velocity and attenuation for a set of natural aquifer samples from the Pinellas site (Geller et al., 2002; Ajo-Franklin et al., 2002, 2003). Samples with a variety of textures ranging from clean sands to clayey silty sands were tested with porosities ranging from 32% to 43%. Only NAPL-to-water injection sequences were performed. The maximum contaminant saturations achieved were less than 80% for all samples. Several auxiliary samples saturated only with water were also characterized to provide added information on the relationship between V_p and textural parameters. Measurements were made in the transmission mode at 500 kHz. Reductions in V_p of up to 12.2% were observed for one sample with a 59% TCE saturation.

4.2. Dielectric properties

In contrast to acoustic measurements, a somewhat larger body of work exists investigating the dielectric signature of DNAPLs in soil and various theoretical models for describing these signatures. All measurements made to date have shown that the replacement of water with a NAPL phase decreases the bulk dielectric constant of the porous composite.

Porokhvoi et al. (1996) used a Rhode and Schwartz ZPV-Z5 S-parameter test set to make frequency domain dielectric measurements (200 MHz–1.2 GHz) on synthetic sand/clay mixtures (77%/23%) using benzene, heptane, xylene, acetone, and toluene as saturating contaminants. The resulting experiments consider contaminant fractions of between 1.15% and 13.8% by weight. Although they observe a reduction in dielectric constant for samples partially saturated with NAPLs, their results are difficult to interpret in terms of fluid effects due to the limited number of saturation levels examined and their simultaneous consideration of several secondary parameters including sand/clay fraction and total fluid saturation.

Santamarina and Fam (1997) measured the complex dielectric permittivity of soil/pollutant mixtures, using benzene, xylene, toluene, tetrachloroethylene (PCE), trichloroethylene (TCE), and chlorobenzene as organic pollutants. Kaolinite and bentonite clays were used to as the porous matrix. Measurements were made between 0.2 and 1.3 GHz using an HP-8752A network analyzer and an HP-85070A dielectric probe. Although significant changes in dielectric properties were noted

in both clays after injection of TCE, the relationship between complex permittivity and TCE saturation was not quantitatively determined.

Persson and Berndtsson (2002) investigated the dielectric properties of synthetic soils partially saturated with sun-flower seed oil (SFSO) using the time domain reflectometry method. Their measurements were performed using a three-prong TDR probe and a Tektronix 1502C cable tester to measure both the dielectric constants and conductivities of homogenized sand/water/NAPL mixtures. They used the Lichtnecker-Roth mixing model with a saturation dependent geometry coefficient to fit their dataset.

Francis and Rinaldi (2003) performed frequency domain dielectric measurements on silica sand, kaolinite, and loess samples partially saturated with paraffin and lubricant oils. Measurements were made using an HP 8752A network analyzer and an HP 85070A dielectric probe at frequencies between 20 MHz and 1.3 GHz. They conclude that both the CRIM and self-similar effective medium models (Gueguen and Palciauskas, 1994; Mavko et al., 1998; Sen et al., 1981) provide adequate prediction of the effects of NAPL saturation on bulk dielectric constants.

Ajo-Franklin et al. (2004) used a coaxial TDR cell to examine the dielectric properties of both synthetic and natural aquifer samples when saturated with mixtures of water and TCE. This experiment was designed to quantify the radar signature of DNAPLs at a DOE field site (Geller et al., 2002; Ajo-Franklin et al., 2002, 2003). They observe reductions in dielectric constant of up to 32% at TCE saturations of only 30%.

Several theoretical studies examine possible Endres and Redman (1993) investigated the consequences of using a modified differential effective medium theory to model the dielectric effects of saturating soils and rocks with various contaminants. Carcione et al. (2003) modeled both the electromagnetic and acoustic properties of NAPL saturated materials using the Bruggeman-Hanai-Sen (BHS) relationship (Schon, 1996; Sen et al., 1981) for dielectric properties and a modification of White's patchy saturation model (White, 1975) for acoustic properties.

5. Conclusion

The acoustic and dielectric properties of dense chlorinated solvents are distinct from fluids naturally occurring in the subsurface. Decades of laboratory experiments have provided us with a wealth of data pertaining to the characteristics of pure DNAPLs. Generally, DNAPLs exhibit high densities (1253 to

1622 kg/m³ @ 20 °C), low P-wave velocities (938 to 1217 m/s @ 20 °C), and low dielectric constants (2.2 to 10.9 @ 20 °C). DNAPL density, P-wave velocity, and dielectric properties are observed to decrease with increasing temperature. No available measurements have examined the geophysical properties of DNAPL mixtures extracted from contaminated field sites; a detailed study on the properties of these more complex fluids would greatly aid the analysis of field data.

More recent experiments have laid the groundwork for understanding the geophysical signatures of DNAPLs within unconsolidated soils. Although almost all of the experiments examined observed changes in bulk properties due to DNAPL saturation, it is unclear whether these variations are of sufficient magnitude to be unambiguously observed in a field setting. Existing studies have shown that DNAPL saturation reduces both the P-wave velocity and dielectric constant of initially water saturated sediments.

Field-scale experiments have already confirmed that GPR and other geophysical methods can track the descent of DNAPLs within the subsurface if the spill site is known a priori (Sander et al., 1992; Redman, 1992; Brewster et al., 1992, 1995; Brewster and Annan, 1994) and sufficient DNAPL volumes are present. However the static detection of DNAPLs is a much more difficult problem due to the non-uniqueness of individual geophysical methods; often lithological changes produce signatures similar to those of contaminants. One possible avenue for improvement is the fusion of various imaging techniques, a process which might enable the detection problem to be successfully resolved.

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